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INVESTIGATION OF THE CHEMICAL COMPOSITION OF THE ATMOSPHERE OF VENUS BY THE "VENERA-4" AUTOMATIC STATION

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16. Abstract

The data transmitted to Earth by the "Venera-4" automatic station during its descent by parachute in the Venusian atmosphere indicate that Venus has less hydrogen than Earth. It is concluded that the greenhouse effect has produced a dense corrosive atmosphere which has leveled the surface of the planet.

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INVESTIGATION OF THE CHEMICAL COMPOSITION OF THE
ATMOSPHERE OF VENUS BY THE "VENERA-4" AUTOMATIC STATION

A. P. Vinogradov, Yu. A. Surkov
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Introduction

After the discovery of the dense atmosphere of Venus in 1761 by M. V.   /244*
Lomonosov, numerous attempts were made to study its characteristics by means of
terrestrial observations. The method of infrared spectrometry proved to be
quite reliable in determining the presence of CO_2 alone, and its content was
estimated by other authors to be everything from a few percent to 100%.
Indications of the presence of other gaseous components (H_2O, N_2, O_2 and others)
have been disputed until the present [1]. The lack of factual material led to
the development of numerous and contradictory models of the Venusian atmosphere,
constructed on the basis of arbitrarily selected suppositions. The flight of
the "Mariner-2" spacecraft past Venus in 1962 did not answer these trouble- |
some questions. It had become quite obvious that only direct measurements of
the basic parameters of the atmosphere could provide a reliable basis for
interpretation of the numerous terrestrial observations and the geochemical
characteristics of the surface of the planet.

The latter is particularly important, since only comparative planetological
data can provide information on the difficult questions of the origin and
conditions of formation of the surface strata of the Earth. The comparison of
the atmospheres of Venus and Earth, so different at first glance, is particularly
interesting.

1. Design of the Experiment

The Venera-4 automatic interplanetary station reached Venus on October 18,
1967 after a flight lasting 128 days; passing through the atmosphere of the

planet, it made the first descent into the lower layers and conducted direct measurements of its parameters.

The principal scientific task of the Venus-4 station was the investigation of the physical-chemical and structural characteristics of the atmosphere of Venus. The station was composed of two main parts: the orbiting section and the lander. The lander weighed 388 kg and was nearly spherical; its diameter was about 1 m. It was equipped with instruments for determining temperature, pressure and chemical composition of the planet's atmosphere. All of the measurements were performed in the atmosphere of the planet as the lander descended by parachute.

The chemical composition of the Venusian atmosphere was determined by gas analysis, using instruments specially developed for this purpose. The lander carried 11 gas analyzers which were arranged in two groups: the first was composed of 5 analyzing units and the second of 6. The gas analyzers were switched on by a programmed timer following deployment of the parachute system. The first group of gas analyzers operated in the Venusian atmosphere at a pressure of approximately 550 mm and the second at approximately 1500 mm. The temperature of the medium in which the measurements were made was 25° ± 10°C and +90° ± 10°C, respectively.

2. Apparatus and Methods of Determination of the Chemical Composition of the Atmosphere

From the numerous possible methods of determining the composition, we selected simple and reliable physical-chemical methods based on well-known reactions with a sufficient degree of selectivity. In order to increase the reliability of the results, both threshold and amplitude sensors with backup systems were employed. Hence, the reliability with which various results were /245 obtained differed slightly and this was taken into account in evaluating the results of the measurements. Some of the gas analyzers consisted of cylinders with a given volume, divided into two compartments by a membrane. One compartment contained a chemical absorber which would absorb the given component. Prior to the measurements, both compartments were evacuated and hermetically sealed. During analysis, the atmosphere was admitted simultaneously into both compartments which were then resealed. In order to determine the basic

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components of the atmosphere, a recording was made of the difference in pressures arising in the compartments as the result of absorption of one of the components. More sensitive physical-chemical methods were used for analysis of components occurring in small amounts in the atmosphere; these methods were based on measurement of the differences in resistance of specially selected chemical absorbers that would take place in different cells, the difference in thermal conductivity of special current-carrying elements, etc. The data from the gas analyzers were used to determine the content of CO_2, N_2, O_2 and H_2O in the Venusian atmosphere. The determinations were carried out over a broad range of possible concentrations in view of the considerable scatter and indeterminacy of the original data as indicated by terrestrial observations.

3. Results of the Measurements

The results of the determination of the chemical composition of the Venusian atmosphere are listed in Table 1. As may be seen from the table, the existence of CO_2 was confirmed by 4 sensors whose readings (in percent by volume) were distributed as follows: more than 1%, more than 10%, more than 30% and 90 ± 10%. Although the error in the determination of CO_2 for the amplitude sensor reached ±10% due to the development of external errors, we tend to think that the CO_2 content in the atmosphere of Venus is at least 90% (acid vapors of HCl, etc., previously detected in the Venusian atmosphere by means of terrestrial observations in amounts less than 0.01% could not affect the results of the measurement).

The nitrogen sensors (using the reaction with metallic zirconium at 1,000°C) twice showed a lack of significant amounts of this gas in the Venusian atmosphere. One negative value was obtained with a nominal threshold sensitivity of the sensor of 7%, the other with a threshold value of 2.5%. In view of the fact that the second determination contained a large relative error (but one which did not overlap the threshold of the first measurement), the threshold of nitrogen content of less than 7% may be considered reliably established by these two measurements. The lower limit (less than 2.5% nitrogen) is less reliable, due to the generally reduced reliability of one negative reading.

The O_2 content was found between the two threshold values of the sensors operating on different principles. In one sensor, a tungsten wire blew out

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instantly at a temperature of approximately 800°C, designed for a threshold of approximately 3 mm partial pressure of oxygen in the volume of the sensor, corresponding to 0.5% of the gas at a pressure of 550 mm. The other sensor was based on the absorption of O_2 by the sublimating vapors of phosphorus; the P_2O_5 which is thus formed is also capable of absorbing water vapor.

The sensor which was set for the threshold value of the absorbed mixture of $H_2O + O_2$ of 1.6%, gave a negative reading. Judging from the data on the joint determination of the mixture of $H_2O + O_2$, as we shall see below, the O_2 content cannot be higher than 1-1.5%.

Water was determined by three sensors. At the upper point (H ~ 26 km) the resistance sensor with P_2O_5, determining the total gaseous and condensed water, gave a H_2O content of more than 0.65 mg/1, corresponding to a value greater than 0.1% or a condensation temperature of more than -22°C. At the lower point (H ~ 20 km) the water vapor content according to the sensor with P_2O_5 was also more than 0.65 mg/1 (more than 0.03%), but according to the pressure sensor with the $CaCl_2$ absorber it was less than 11 mm (less than 0.7%), corresponding to the condensation temperature being less than +15°C. Since the instrument had a temperature of at least 25°C at this time, the pressure loss due to vapor /246 condensation in the instrument must be recognized as quite insignificant and we may conclude that the true upper limit of H_2O vapor was determined.

Hence, the possible range of vapor pressures in different levels of the Venusian atmosphere lies between ~0.65 and 11 mm, which corresponds to the condensation temperatures at -22° and +15°C. From this it follows that the existence of a liquid-drop form of water is only possible in the cloud layer, inasmuch as the conditions on the Venusian surface (temperature of +280°C ~ 20 atmospheres) are far above the limits within which liquid water could exist.

Summing up the general results of the analyses, we can assume the following composition of the Venusian atmosphere (in % by volume): CO_2 — 90 ± 10% (probably more than 90%); O_2 more than 0.4% and less than 1.5%; N_2 less than 7% (possibly less than 2.5%); H_2O — 1-8 mg/1 [2, 3].

As we can see from these results of the research, this composition excludes the important role of other gases which has been suggested by other researchers.

However, the presence in the Venusian atmosphere of small amounts of argon and other rare gases is not excluded. Knowing the total composition of the atmos- phere will make it possible to calculate certain possible equilibrium impurities that arise as the result of photochemical reactions. On the whole, the atmosphere of Venus has been found to be oxidative and most similar to the hotbed model [2].

4. Evaluation of the Results

One of the principal problems linking the astronomical and geological sciences is the method of formation of the Earth and planets and their further differentiation into principal shells — atmosphere, hydrosphere, lithosphere, mantle and so forth.

The question is one of whether this formation took place at the time of the creation of the Solar System from hot stellar matter, or whether the process of differentiation took place in the geological period of existence of the planets in the Earth group, which were formed from cold chemical materials similar to the material from which meteorites are made.

The idea of the existence of a "primordial", "primitive", "dense", "residual" atmosphere, composed of the gaseous component of the protoplanetary cloud was long connected with the formation of the planets. According to these theories, the substance of the planets condensed from the "hot" stellar material — hot plasma. As the liquid-molten bodies cooled, the vapor and gas condensed and finally fell in the form of precipitation onto the solidifying surface of the Earth, forming the "primordial" ocean and hydrosphere and the "primordial" atmosphere. However, the geochemical study of the oldest rocks in the Earth's crust and the isotopic investigation of the inert gases in the atmosphere have dealt a fatal blow to these theories.

As we know, most scientists feel that the planets were formed from cold cosmic substance through agglomeration of the latter. Volatile substances formed part of planets, bound up with solid material, which caused their accumulation at the periphery of the Solar System under extremely low temperature conditions.

TABLE 1. RESULTS OF THE CHEMICAL ANALYSIS OF THE ATMOSPHERE OF VENUS

Condition of Analysis	Component Determined	Type of Sensor	Principle of Operation of Sensor	Measurements (in % by volume)	Limit of Measurements (in % by volume)
First Group of Analyzers $P \sim 550$ мм $t \sim 25° \pm 10°$ C	CO_2	Threshold	Thermal Conductivity	Threshold 1%	Greater than 1%
	CO_2	Amplitude	Absorption of KOH	7-100%	$90 \pm 10\%$
	N_2	Amplitude (z_n at 1000° C)	Following absorption of CO_2 and O_2 - Absorption of N_2	7-100%	Less than 7%
	O_2	Threshold	W (melting of a wire at 800° C)	Threshold 0.4%	More than 0.4%
	H_2O	Threshold	Wetting P_2O_5, Measurement of electrical conductivity	Threshold 0.1%	More than 0.1%
Second Group of Analyzers $P \sim 1500$ мм $t \sim 90° \pm 10°$ C	CO_2	Amplitude	Absorption of KOH	2-30%	Above 30%
	CO_2	Threshold	Absorption of KOH	Threshold 1%	More than 1%
	N_2	Amplitude	Following absorption of CO_2 and O_2 - Absorption of N_2 (z_n at 1000° C)	2.5-50%	Equal to or less than 2.5%
	O_2 ($+ H_2O$)	Threshold	Evaporation of phosphorus	Threshold 1.6%	Less than 1.6%
	H_2O	Threshold	Wetting P_2O_5, Measurement of electrical conductivity	Threshold 0.05%	Above 0.05%
	H_2O	Amplitude	Absorption of $CaCl_2$	Threshold 0.7%	Less than 0.7%

The atmospheres of the terrestrial planets are secondary formations which arose as the result of subsequent degassing of the initial solid material of the planets, similar in composition to that which is found in meteorites today. This degassing takes place as the result of low heating of the planets, whose material passes through a zone of high temperatures similar to the processes involved in zone melting, causing differentiation of material in accordance with the criterion of fusibility [3]. The surface of the planet itself can serve as such a local zone melting area, during whose growth point foci of heating

develop as meteoritic bodies fall [4], but secondary heating of its core is the primary source of heat in the geological stage of existence of a planet, caused by the compressive energy of gravitation and primarily the influence of heat generated by radioactive elements. It is true that the substance of the planet does not pass through a heated zone, but the molten zone which develops in the depths moves up from the depths toward the surface, transforming a quantity of material which is many times greater than the volume of the molten zone. Under the influence of this heating, a one-way separation of the material composing the planet into shells takes place. The mechanism of this grandiose process of melting and degassing of the Earth's mantle was duplicated experimentally by us [5].

Hence, the total amount of volatile substances given off in the course of evolution of a planet depends upon their initial concentration in the solid material of the planet (which may be linked to the differentiation of the protoplanetary substance as a function of the distance from the Sun) and the nature of the endogenic processes taking place within the planet following its formation. As we know, the volatile fraction which separates during melting and degassing of the mantle contains cosmic, radiogenic and other gases.

H_2O makes up most of the highly volatile substance on Earth. This fact is explained not only by the abundance of water during the formation of the Earth but also by the fact that H_2O (with other conditions being equal) is absorbed to a greater extent by molten silicates than other vapors and gases, for example, CO_2. In addition to H_2O, many other gases that are soluble in water were given off, such as for example HCl, $B(OH)_3$, $(NH_4)_2CO_3$, some of the compounds of sulfur and other gases that are slightly soluble in water — such as inert gases and CH_4, CO_2 to some extent and so forth.

Formerly, the total amount of fluid substances and gases that were separated out on the surface of the Earth in the course of the melting of the basalt base of the crust was referred to as the special planetary fraction [6] which was produced both as the result of volcanic processes and in the regional degassing of the Earth.

The subsequent fate of this special volatile plentary fraction depended upon the physical-chemical (thermodynamic) conditions on the surface of the

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planet and was governed by the exogenic processes taking place at that time. Under these conditions processes of secondary reactions developed between substances that governed their form of occurrence, either in the gaseous (atmosphere), liquid (hydrosphere) or solid (lithosphere) state. From the relationships between the rates of endogenic degassing of the planet and the dissipation of its gaseous shell, the total amount of volatile substances was created which can be found today on the surface of the planet.

Hence, a detailed study of the atmospheres of the planets, or more precisely the "special planetary fraction" which we mentioned earlier, provides some idea about a great many geochemical processes forming the planet.

In this connection, let us examine the relationship between the principal components that determine this fraction for the Earth and Venus. This is particularly interesting, first of all, due to the close relationship between these planets in terms of size and secondly because the total amount of degassed products for the two planets, as we can see from the results of our research, is the same (within the limits of half an order) with the exception of hydrogen.

As we know, the carbon in the Earth's crust is mainly bound up in the carbonates of sedimentary rocks and makes up about $2 \cdot 10^{23}$ g of CO_2. If all of the CO_2 from the carbonates and the hydrosphere of the Earth were to be released into the atmosphere, the mass of the latter ($5 \cdot 10^{21}$ g) would increase approximately 40 times, i.e., in other words, the gas pressure would be about 40 atmospheres. The total quantitative correspondence between Venus and the Earth could be achieved under the condition that we assume that about one-half of the possible CO_2 content occurs on Venus in the lithosphere in the bound state, and the rest in the atmosphere[2].

The conditions of carbonate-silicate equilibrium on Venus are such that the carbonates of magnesium and calcium must begin to decompose at temperatures about 300°C. The conditions of this equilibrium have been studied repeatedly and have been put forward to explain the increased amount of CO_2 in the atmospheres of the planets.

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[2]It has subsequently been established that the Venus-4 station did not reach the solid surface of the planet; a recalculation shows a higher atmospheric pressure and a lower amount of bound CO_2.

The source of nitrogen in the Venusian atmosphere must clearly be considered to be NH_4^+ which is degassed by volcanoes on Earth primarily in the form of NH_4Cl, which is sublimated at 350°C. On Venus, due to the tremendous amount of CO_2, $(NH_4)_2CO_3$ must be formed, which easily breaks down at 58°C to form free ammonia. The molecule of NH_4Cl is rather strong, while NH_3 oxidizes easily to form N_2 in the presence of oxygen. It is probable that this method constitutes the basic method of formation of nitrogen in the Venusian atmosphere. This process is of interest because it assumes the presence of a small amount of ammonium salts in the cloud layer of Venus, and subsequent studies will concentrate on detecting the latter.

Without a doubt, one source of the traces of free oxygen in the atmosphere is the process of photochemical decomposition of water in the upper layers of the atmosphere which has been thoroughly studied under terrestrial conditions and becomes effective under conditions of evaporation of hydrogen.

If we assume that the probable nitrogen content is about 2% and the O_2 content about 0.5%, simple multiplication by a pressure of 40 atmospheres will give the same total amount of nitrogen and oxygen in the atmosphere of Venus as on the Earth (78% and 21%, respectively).

If we assume that the N_2 content of less than 2.5% as determined by one reading is correct, this will correspond in all respects to the idea of the possible presence of salts in the lithosphere and cloud layer of Venus. All these coincidences can hardly be pure chance. Instead, they indicate that the endogenic processes, i.e., the melting of the substance forming the crust and the processes of degassing of planets of equal size, proceed along similar paths and only the subsequent history of the atmosphere changes their appearance as a function of proximity to the Sun, mass of the planet, determining the degree of dissipation of the atmosphere and other exogenic factors.

An important gap in this similarity of the special planetary fraction on the Earth and Venus is the shortage of water observed on Venus. In fact, however, if we estimate the total amount of liquid water condensed in the dense clouds of Venus, it will be far less than the total mass of the hydrosphere of the Earth (about $2 \cdot 10^{24}$ g). The stable existence of liquid water on the surface

of Venus is impossible because the temperature of the latter is much greater than the boiling point of water under these conditions (about 200°C).

There may in fact be a significant amount of water on Venus, in the bound state, in the form of different types of hydrosilicates, but they will be thermodynamically unstable and cannot contain a sufficient amount of water.

Hence, a general hydrogen deficit definitely exists on Venus in comparison with the Earth, which is supported by the relatively weak hydrogen corona which was observed by the Venus-4 interplanetary station.

Hydrogen, as the most mobile of all elements, generally is very scarce in the free state on all planets of the Earth group in comparison with its distribution in space. The Earth, with its hydrosphere, is the sole exception where larger residues of hydrogen can be found.

The cosmochemical history of hydrogen is largely unclear, and the reason for this discrepancy may be found in three processes:

1) a possible loss of hydrogen into circumsolar space in the preplanetary stage of development of this system, which may be traced in order from Mercury to the terrestrial planets (Venus, Earth), the giant planets and the comets;

2) the process of dissipation of hydrogen, formed as the result of photochemical decomposition of water, which is undoubtedly going on and more intensively near the Sun;

3) the least studied (but possibly most interesting) problem of the relationship between the hydrogen content and the magnetic field of a planet. The current hydrogen content (water) in the upper atmosphere of planets is the result of two opposing processes: dissipation and capture of protons from the solar wind and chemical radiation with formation of atomic hydrogen. The powerful magnetic field of the Earth, in contrast to the very weak magnetic field of Venus (and Mars) considerably changes the conditions of capture and loss of charged particles in the upper atmosphere of the planet. It is possible that it is precisely this process that is responsible for the stability of the hydrosphere of the Earth within geological time.

If this is really so, the three principal characteristics of the Earth enjoy a cause-effect relationship with one another: the existence of a magnetic field ensures the existence of a hydrosphere, without which organic life would be unthinkable.

The general picture of the evolution of the atmosphere of Venus can be represented as follows.

Due to the closer proximity of Venus to the Sun, its equilibrium temperature is above 50°C. Aside from other factors, this is due to the transition of water and hydrocarbons in significant amounts into the Venusian atmosphere. The occurrence of water and hydrocarbons in significant amounts has in turn produced an enormous degree of absorption of solar heat by the atmosphere, thus leading to a significant photodissociation of water and the hydrocarbons with a lack of a sufficient protective effect of nitrogen and oxygen in the atmosphere and its high temperature. The oxygen which was formed was absorbed by the rocks on the surface of Venus. CO — the product of photodissociation of hydrocarbons — was not retained and recombined with CO_2, due to the presence of oxygen from the conjugation reaction — photodissociation of water. Under high temperature conditions such as those that exist on the surface of Venus and the lack of a magnetic field, the hydrogen dissociated. All of this led to spontaneous heating of the atmosphere and the development of the greenhouse effect. It is possible that a certain share of the heat came from the core of the planet. When the temperature of the surface of the planet Venus reached approximately 250-300°C, a great many carbonates reacted with silicates, giving off a tremendous amount of carbon dioxide into the atmosphere. It follows from these data on the temperature and pressure of the atmosphere on Venus that water must boil at a temperature above 200°C, i.e., it cannot form a hydrosphere. Hence, the Earth and Venus are very similar in terms of their endogenic processes. However, the exogenic processes which depend primarily upon the surface temperature (i.e., the proximity to the Sun) have led to the formation of different atmospheres. As the result of the autoregulatory processes taking place on the surface of Venus, conditions have led to the formation of a dense atmosphere. Under these conditions, the surface rocks of Venus must have been subjected to severe decomposition. The existence of such an aggressive atmosphere under

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conditions of intensive movement probably caused a leveling of the surface of the planet.

Evidently, we are dealing here with a case of stepwise changes in the equilibrium composition with establishment of a new equilibrium and an insignificant change in the initial conditions, similar to the way in which the climate of the Earth changes during periods of glaciation and in a number of autoregulatory processes.

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